University of Colorado Boulder

Karl G. Linden, Ph.D., Helen and Huber Croft Professor
Department of Civil, Environmental, and Architectural Engineering
College of Engineering and Applied Science
428 UCB, 1111 Engineering Center
Boulder, CO 80309-0428

Telephone: 303.492.4798
Fax: 303.492.7317
http://ceae.colorado.edu/klinden
email: karl.linden@colorado.edu

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Melenee Emanuel
Environmental Scientist
State Water Resources Control Board, Division of Water Quality
Waste Discharge Requirements – Policy
Sacramento, CA 95812 - 0100

Re: Peer review of the Draft Amendment to the State of California Water Board's Recycled Water Policy

Dear Melenee,

The attached report provides a determination, in my expert opinion, for the scientific basis of the proposed regulatory action outlined in the Draft Amendment to the Recycled Water Policy. The report focuses comment on my specific areas of expertise in environmental engineering related to the Draft Amendment including (1) the list of CECs; (4) performance indicator CECs; (5) monitoring treatment process performance; (6) validity of percent removal; and (8) phased monitoring approach. Information on the other topics was also reviewed and an opinion provided in the text below.

In preparation for this report, I received and reviewed materials including:

Attachment 1: Summary of Monitoring Requirements for Constituents of Emerging Concern for Recycled Water.
Attachment 2: Scientific Issues to be Addressed by Peer Reviewers.
Attachment 3: List of Participants.
Attachment 4: List of References (provided on CD), referring to specific references where needed.
Attachment 5: Draft Amendment: Requirements for Monitoring Constituents of Emerging Concern for Recycled Water.
Attachment 6: The revised Recycled Water Policy will be provided upon Peer Review.
Final Report: Monitoring Strategies for Chemicals of Emerging Concern (CECs) in Recycled Water

The report will follow the order of topics suggested in Attachment 2: Scientific Issues to be Addressed by Peer Reviewers. Please contact me with any questions or clarification required.

Sincerely,

Karl Linden, Ph.D.
Helen and Huber Croft Professor of Environmental Engineering

1) Sufficiency of potential water contaminant lists of CECs.

The approach taken by the team to develop the list of possible CECs to monitor for was rational and sound. This includes the process for the USEPA CCL3 list selection, the UCMR and the California (CDPH) unregulated notification compounds. The team also considered what appears to be a limited set of peer-reviewed publications and reports, mainly those authored by the Panel Members of the Final Report. It was recommended in Section 9 (Recommendations) of the final report that additional peer-reviewed studies be evaluated to better populate a database of CECs likely to occur in recycled water and include studies outside of California. It is not clear that the final list in Table 1 of the draft amendment includes any additional studies beyond those reviewed by the Panel Members.

In the "Draft Amendment" it states "An indicator CEC is an individual CEC used for evaluating a family of CECs with similar physicochemical or biodegradable characteristics". This point is also made in the Final Report. However, it was not clearly discussed or reported in either the Final Report or the Draft Amendment, the specific chemical/physical characteristics of the chemicals (i.e., octanol-water coefficient, henrys constant, etc.) and what "family" of CECs this chemical represented with regard to these physiochemical or biodegradable characteristics.

The list of CECs is also important regarding the potential to monitor for CEC removal across the types of treatment processes utilized. Since advanced oxidation processes are part of the treatment train recommended in CA, it is also important to address transformation products, such as oxidation byproducts. While these transformation products are noted as "unknown knowns" by the Panel, it could be argued that they should be "unknown unknowns", as the combination of background water constituents, CECs, and oxidation could form not just breakdown products (which may be considered unknown knowns), but also new products that would not necessarily be recognizable from a known parent compound.

While the list of CECs to be monitored may be comprehensive and certainly follow from the suggestions of the Panel Members in the Final Report, this reviewer feels that the Table 1 should also include information on the range of physiochemical and biodegradable characteristics of these chemicals to illustrate that it is indeed a broad enough list to cover a range of both performance and health-based chemicals of similar structure and function. Furthermore, it is important to note that changes in water quality such as pH and possibly organic matter characteristics, can affect the physiochemical properties of some chemicals and therefore impact the removal performance and health based impacts. Such water quality induced changes, if known for these CECs selected, should be reported, and may be indicated by characteristics such as pka.

2) Appropriateness of the approach for selecting CECs of toxicological relevance to monitor for recycled water uses.

While not my area of expertise, a few points will be made. It is agreed here, that the Panel's comment on the predominantly negative findings of the combined epidemiological and other toxicological studies provide concordant evidence that recycled water is a safe source of water for drinking water supplementation. It is also prudent that the lack of heretofore-positive findings does not negate the need for continued monitoring of recycled water for safety.

The approach for selecting monitoring trigger levels (MTLs) was reviewed and nothing of concern to this reviewer was noted. The approach for comparing CEC90th percentile MEC to the MTL and selecting candidates for monitoring was sound. Agreed that only CECs with robust analytical methods should be selected for monitoring, however, priority should be made for any CEC that meets thresholds for monitoring but does not yet have a robust method, for method development to be encouraged.

3) Determination of initial MTLs for the landscape irrigation

No disagreement with this approach.

4) Adequacy of selected performance indicator CECs

Performance indicators are essential for monitoring the treatment processes in place to remove CECs. The stated intent of the performance indicators is that "the absence or removal of an indicator constituent during a treatment process would also ensure absence or removal of unidentified chemicals with *similar properties*." These properties are assumed to be similar to those described in Table D-12 in the Final Report, such as octanol/water coefficient, henrys constant, soil-water partition, etc., all properties which could be affected also by pH. While the list of performance based indicators is presented in Table 8.2 in the final report and in Table 1 in the Draft Amendment, there is no discussion on the range of properties that these indicator chemicals have anywhere in the Final Report or Amendment. Therefore, without looking into the literature it is not possible to know if the properties of the chemicals to serve as indicators represent the universe of CEC of interest to the State of CA. It would be helpful if these properties and some discussion on them and how they represent the CEC universe was included somewhere for the public.

Adequacy of the selected performance indicators would also necessitate an understanding of the extent to which these chemicals were removed in the proposed treatment processes for reclaimed water. Specifically, performance information for membrane treatment and UV-advanced oxidation should be included in the report. Some of this material is available in Dickenson et al., 2009, but in the supplemental information section.

Based on pilot and full-scale studies (Drewes et al., 2010a; Dickenson et al., 2009 – which appear to be the same data from the same study) following RO treatment, atenolol, trimethoprim, gemfibrozil and meprobamate were noted as good performance indicators of UV/H2O2 AOP. Note that this is only specified for when the UV/H2O2 processes follow RO – those chemicals that remained in the water post – RO were the only ones that could be tested. Another good indicator noted was NDMA. NDMA is a good indicator for UV photolysis, not necessarily for AOP in a UV/H2O2 process, but this is not pointed out anywhere in the report.

One final comment on this section is on the statement that "the absence or removal of an indicator constituent during a treatment process would also ensure the absence of removal of unidentified chemicals with similar properties". I would disagree that the absence of one compound ensures the absence of other chemicals because it is possible that the indicator compound was never there and if no other similar compounds were monitored for, you cannot say that other compounds with similar properties would also be absent.

5) Adequacy of the selected surrogates for monitoring treatment process performance

Surrogates can only represent performance if they are good predictors of the behavior of CECs through a specific treatment process. The surrogates noted for direct injection reuse should be specifically suited for RO + UV/H2O2 treatment, as this is the standard used in California for ground water recharge/reuse. Thus each surrogate should be noted for what process it is best to monitor for. Apparently the only surrogate adequate for UV/H2O2 is UV absorbance (UVA), based on the information provided in Dickenson et al., 2009 (supplemental information) and Drewes, et al., 2008. Most of that publication on advanced oxidation is for ozone based advanced oxidation, not UV based advanced oxidation. While UVA is the only surrogate for UV/H2O2 applications, it did correlate well with the removal of a few indicator compounds that made it through RO to the UV system (Drewes et al., 2008). Interestingly however, this surrogate is not indicated for direct injection applications (it is for SAT treatment). More on this later under question 6.

It is suggested that more information be provided as to what surrogates are good for what treatment process, otherwise, they may be used incorrectly. Section 8.3 in the report touches on this issues and prescribes a process to determine which indicator compounds and surrogates may be important to monitor, but it does not explicitly state the appropriateness of each indicator or surrogate for monitoring the operational performance of a treatment process.

In the draft amendment it states:
"Performance indicator CECs and surrogates detected during the baseline phase and that exhibited reduction by a unit process and/or provided an indication of operational performance shall be selected for monitoring of standard operations."

While this is generally a logical approach, this logic suggests that only some of the performance indicators may be monitored over time, depending on what is found in the baseline phase. It is conceivable that those compounds detected during the baseline phase that are selected for study, are not ideal indicators for a specific treatment process. There may want to be some specific compounds that are known to be good indicators for a specific treatment process (such as NDMA for UV/H2O2) to be required for longer term monitoring, even if they are not selected from the baseline monitoring phase.

6) Validity of expected percent removal of surrogates and performance indicator CECs for a treatment process

The percent removals for performance indicators and surrogates are provided in the panel's Final Report in Table 8.2. These percent removals are indicated for both groundwater recharge (SAT) and direct injection. For performance indicators, these span a good range of compounds with varying removal percentages. The surrogates are listed as ammonia, nitrate, DOC and UVA for SAT and conductivity and DOC for Direct Injection. While these surrogates may be appropriate for the SAT treatment, the surrogates for direct injection, specifically those indicating AOP treatment efficacy, do not seem appropriate. While both conductivity and DOC would readily indicate RO performance, they do not indicate AOP performance. UVA could be a good surrogate for AOP but it is not clear how much UVA would remain in the water as an indicator after RO. The performance indicators could provide a means to indicate AOP treatment as NDMA would be transmitted through the RO and be available to AOP as an indicator.

7) Appropriateness of tiered risk quotient thresholds and corresponding degree of response for evaluating monitoring results for health-based CECs in recycled water

Based on my limited expertise in toxicology, the approach presented by the panel in the Final Report appeared appropriate and rational.

8) Adequacy of monitoring frequencies for CECs and surrogates and the phased monitoring approach

In my professional judgment, the program for monitoring was well thought out and is a rational approach for the industry to move forward in confidence. For specific CECs, the ideas of an initial (quarterly) assessment phase, a baseline monitoring phase, and a standard operating monitoring plan of semi-annual or annual monitoring is adequate and not overly onerous on the utility. The surrogate monitoring plan is also sound as it exploits the possibilities of continuous monitoring for these surrogates where this is possible and reasonable, and recognizes the value in monitoring of the treatment process, as opposed to just the presence or absence of CECs.

9) Additional consideration for the peer reviews
Based on my limited knowledge of toxicology, I thought the MTL derivation approach was sound.

The Big Picture

A few comments below on some specific scientific issues that were not well described, or not seen, in the material received. Taken as a whole, the scientific portion of the proposed rule is state of the art and should move forward in confidence. Furthermore, the proposed Draft Amendment is a document that strongly draws on the panel's Final Report and provides a robust mechanism for monitoring of CECs in recycled water for years to come.

Specific comments not addressed:
1) On page 2 of the draft amendment it is stated that:
"AOPs are treatment processes involving the use of hydrogen peroxide and ozone; commonly combined with ultraviolet light irradiation."
This is not completely correct. AOPs typically are either UV/H2O2 or ozone/H2O2. Ozone/UV and ozone/H2O2/UV are also AOPs but are rarely used in recycled water applications. So saying they are commonly combined with ultraviolet light irradiation is not correct. The most common AOP used in the water industry is UV/H2O2 advanced oxidation, such as in the Orange County GWR project. It was my understanding that this technology, preceded by RO, was the treatment train used for direct injection according to the Policy under review.

2) Page 3 of the Draft Amendment and Table 1.
The reporting limits noted may be temporal – they may improve with time. Is there a means to address changes in analytical chemistry that could affect the levels of reporting and how low would it have to be for it to be inconsequential?

On this page it is stated that the list of health-relevant CECs for monitoring may be revised based on baseline monitoring results. Is there a process for this? What would trigger a revision? Would it go back to the universe of chemicals or just evaluate single chemicals? How would new chemicals be identified if only the listed ones are being monitored for?

3) Surrogate issues
The discussion about surrogates on Page 5 says surrogates should be based on the types of treatment used. It would make sense then to indicate for the surrogates listed in Table 2, what treatment processes they can be used for.

4) Performance Indicators
Page 9 discussed performance indicators and states that performance indicators detected during the initial monitoring phase should be used in the baseline monitoring phase. These performance indicators may or may not be the best for monitoring of treatment processes. It may be better to require specific performance indicator(s) that are known to be relevant for a given treatment process.

5) Monitoring framework
It may be instructive to have a flow chart for the monitoring framework.

6) Table 4: All CEC and indicator analyses are semi-annually. While I am not opposed to this, could there be any seasonality to the presence of CECs or performance indicators? How would this be captured?

Is the monitoring phase specifically to correlate the surrogates and CECs or performance indicators? The section on page 66-67 of the Final Report suggests that differentials should be documented during monitoring and somewhat implies that there is more to learn during the monitoring phase about how surrogates and performance indicators correlate for removal during treatment. Yet the Table 8.2 specifies surrogates and indicators and % removals expected. To what extent is this an iterative process as more is learned? I believe the approach is healthy for the industry but the specific intent was not very clear.

7) AOP definition
The Draft Amendment continually refers to "AOPs". However, there are many types of AOPs. Page 2 refers to ozone, peroxide and UV combinations. The draft criteria as quoted in Appendix E of the Final Report, specifies UV/AOP for direct injection applications.
It would be helpful to clean this up and specifically state what types of AOP are acceptable and if it is only UV/H2O2 AOP then it should be stated specifically.